Indian J. Phys. **77A (3)**, 247–253 (2003)

AN INTERNATIONAL JOURNAL
IJPA

Strain field due to transition metal impurities in Cu

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Received 6 May 2002, accepted 11 November 2002

Abstract : The strain field due to substitutional transition metal impurities in Cu metal are investigated using the discrete lattice model using Kanzaki lattice static method. The effective ion-ion interaction potential due to Wills and Harrison is used to evaluate dynamical matrix and the impurity-induced forces. The results for atomic displacements due to 3*d*, 4*d* and 5*d* impurities (Co, Ni, Pd, Ag, Pt and Au) in Cu are given up to 20 NN's of impurity and these are compared with the available experimental data which are found in agreement. The lattice shows expansion due to Co, Pd, Ag, Pt and Au impurities and contraction due to Ni impurity. The maximum displacements of 2.3% of 1 NN distance are found for CuAu alloy, while the minimum displacements of 0.43% of 1 NN distance are found for CuNi alloy respectively. The relaxation energies for Ni and Pd impurities are found less than others impurities in Cu, therefore these impurities may easily be solvable in Cu.

Keywords : Strain field, transition metal dilute alloys, point defects and Kanzaki method

PACS Nos. : 61.72.Ji, 62.20.–x

1. Introduction

The transition metal (TM) based alloys are technologically important and the properties of these alloys are largely influenced by structure and electronic nature of the host and impurity atom. A large number of experimental techniques has been used to study the properties of these alloys. With the advance of synchrotron radiation, absorption spectroscopy has emerged as an additional tool for study of the TM based alloys. Recent data of X-ray absorption fine structure (XAFS) [1] about the transition metal based dilute alloys are of immense importance and due to growing interest in the experimental study of these alloys with the advancement in the experimental techniques has surfaced the need to study the dynamical behavior of these alloys theoretically. This would help in understanding of the transition metal alloy formation. We had used the Kanzaki lattice static method [2] to investigate the strain field due to transition metal impurities in *bcc* transition metals vanadium, chromium and iron [3–5] and *fcc* transition metals nickel and palladium [6]. The effective ion-ion interaction potential due to Wills and Harrison [7] was used to calculate the Kanzaki forces. The calculated atomic displacements of NN's of impurities in V, Fe, Ni and Pd hosts exhibited the same trend as predicted by X-ray diffraction studies for the fractional change in the lattice parameter. Since the data of atomic displacements calculated in the discrete lattice model are of vital importance to study the elastic and electronic properties of dilute alloys [8–11], it is interesting to report the calculations for strain field due to transition metal impurities in *fcc* Cu using discrete lattice model. The plan of the paper is as follows : The necessary formalism is given in Section 2. The calculations and results are presented in Section 3 and discussed in Section 4.

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2. Formalism

For a perfect crystal with self consistent pair potential $\phi(r)$, the total interaction energy Φ_0 is given as

$$\Phi_0 = \sum_n \phi(\boldsymbol{R}_n^0), \tag{1}$$

where $\boldsymbol{R}_n^0$ is the equilibrium position of the n-th host atom. If an impurity is introduced at the origin, the lattice gets strained, and the host atoms move to new equilibrium positions $\boldsymbol{R}_n = \boldsymbol{R}_n^0 + \boldsymbol{u}(\boldsymbol{R}_n^0)$, where $\boldsymbol{u}(\boldsymbol{R}_n^0)$ are the atomic displacements. Kanzaki assumed that these atomic displacements are produced by an appropriate distribution of external forces in the crystal which depend upon the nature of the impurity. The potential energy of the strained lattice under applied external forces is expanded in powers series of the displacements which in the harmonic approximation is given as

$$\Phi = \Phi_0 - \sum_{n,\alpha} u_\alpha(\boldsymbol{R}_n^0) F_\alpha(\boldsymbol{R}_n^0) + \frac{1}{2}\sum_{n,\alpha}\sum_{n',\beta} u_\alpha(\boldsymbol{R}_n^0) u_\beta(\boldsymbol{R}_{n'}^0) \phi_{\alpha\beta}(n,n'), \tag{2}$$

where Φ_0 is the potential energy of the perfect lattice, the force components

$$F_\alpha(\boldsymbol{R}_n^0) = -\frac{\partial \Phi}{\partial u_\alpha(\boldsymbol{R}_n^0)}_{u_\alpha(\boldsymbol{R}_n^0)=0} \tag{3}$$

and the force constants

$$\phi_{\alpha\beta}(n,n') = \frac{\partial^2 \Phi}{\partial u_\alpha(\boldsymbol{R}_n^0)\partial u_\beta(\boldsymbol{R}_{n'}^0)}_{u_\alpha(\boldsymbol{R}_n^0)=u_\beta(\boldsymbol{R}_{n'}^0)=0}. \tag{4}$$

Here, α, β (x, y, z) denote the Cartesian components. $F_\alpha(\boldsymbol{R}_n^0)$ is the α component of the external force applied on the atom R_n^0 and $\phi_{\alpha\beta}(n,n')$ are the force constants which obey the crystal symmetries. The equilibrium values of $u(R_n^0)$ are obtained by minimizing Φ with respect to $u_\alpha(R_n^0)$ *i.e.*

$$\frac{\partial \Phi}{\partial u_\alpha(R_n^0)} = 0. \tag{5}$$

Substituting eq. (2) in (5), one finds

$$F_\alpha(\boldsymbol{R}_n^0) = \sum_{n',\beta} \phi_{\alpha\beta}(n,n') u_\beta(\boldsymbol{R}_{n'}^0). \tag{6}$$

Evidently, the displacements can be evaluated if $F_\alpha(\boldsymbol{R}_n^0)$ and $\phi_{\alpha\beta}(n,n')$ are known.

In the Kanzaki lattice static method, the displacements are expanded in normal coordinates as

$$u_\alpha(\boldsymbol{R}_n^0) = \sum_{\boldsymbol{q}} Q_\alpha(\boldsymbol{q}) \exp\left(i\boldsymbol{q}.\boldsymbol{R}_n^0\right), \tag{7}$$

where $\boldsymbol{q}$ is a wave vector and the expansion coefficients $Q(\boldsymbol{q})$ are normal coordinates. Since we are considering a periodic superlattice of defects, the wave $\boldsymbol{q}$ must satisfy periodic boundary conditions, and all such physically distinct $\boldsymbol{q}$ vectors will be contained within the first Brillouin zone $Q(\boldsymbol{q})$ are in general, complex and to ensure the reality condition for displacements

$$Q(-\boldsymbol{q}) = Q^*(\boldsymbol{q}), \tag{8}$$

where the asterisk stands for the complex conjugate. Using eq. (7) in eq. (2), one gets the Fourier transform of the total energy Φ of the strained lattice as

$$\Phi = \Phi_0 - \sum_{\alpha,\boldsymbol{q}} F_\alpha(\boldsymbol{q}) Q_\alpha(\boldsymbol{q}) + \frac{N}{2}\sum_{\alpha\beta}\sum_{\boldsymbol{q}} \phi_{\alpha\beta}(\boldsymbol{q}) Q_\alpha(\boldsymbol{q}) Q_\beta(\boldsymbol{q}), \tag{9}$$

where $F_\alpha(\boldsymbol{q}) = \sum_n F_\alpha(\boldsymbol{R}_n^0)\exp\left(i\boldsymbol{q}.\boldsymbol{R}_n^0\right)$, (10)

and $\phi_{\alpha\beta}(\boldsymbol{q}) = \sum_{n-n'} \phi_{\alpha\beta}(n-n')\exp\left[-i\boldsymbol{q}.\left(\boldsymbol{R}_n^0 - \boldsymbol{R}_{n'}^0\right)\right]$ (11)

N is the number of unit cells in the crystal $F_\alpha(\boldsymbol{q})$ and $\phi_{\alpha\beta}(\boldsymbol{q})$ are the Fourier transforms of $F_\alpha(\boldsymbol{R}_n^0)$ and $\phi_{\alpha\beta}(n-n')$, respectively. The equilibrium condition in Fourier becomes

$$\frac{\partial \Phi}{\partial Q_\alpha(\boldsymbol{q})} = 0$$

which in conjunction with eq. (9) gives

$$\sum_\beta \left[N\phi_{\alpha\beta}(-\boldsymbol{q}) Q_\beta(\boldsymbol{q}) - F_\beta(\boldsymbol{q})\delta_{\alpha\beta}\delta_{-\boldsymbol{q}\,\boldsymbol{q}}\right] = 0. \tag{13}$$

Eq. (13) gives three simultaneous equations for three components $Q_\beta(\boldsymbol{q})$ for each value of $\boldsymbol{q}$. If $\phi_{\alpha\beta}(\boldsymbol{q})$ and $F_\beta(\boldsymbol{q})$ are known, eq. (13) can be solved for $Q(\boldsymbol{q})$ which, in turn, gives $u_\alpha(\boldsymbol{R}_n^0)$ from eq. (7).

For a central ion-ion potential, the dynamical matrix is written as

$$\phi_{\alpha\beta}(n) = \frac{\partial^2 \phi}{\partial r_\alpha \partial r_\beta}\Big|_{r=R_n^0} = \frac{R_{n\alpha}^0 R_{n\beta}^0}{\left|\boldsymbol{R}_n^0\right|^2}(A_n - B_n + \delta_{\alpha\beta} B_n), \tag{14}$$

where $A_n = \frac{\partial^2 \phi}{\partial r^2}\Big|_{r=R_n^0}$, $B_n = \frac{1}{\left|\boldsymbol{R}_n^0\right|}\frac{\partial \phi}{\partial r}\Big|_{r=R_n^0}$. (15)

In the metallic crystal, the ions are screened by the conduction electrons thereby decreasing the ionic potential faster, which exhibit oscillatory behavior at large distances

It has been found that in the *d*-band metals, the screening is large [8–10]; therefore, the major contribution to $\phi_{\alpha\beta}(q)$ and $F_\alpha(q)$ in these metals is expected to arises from the first few NN's. Including the interactions up to 1NN's, $\phi_{\alpha\beta}(q)$ for the *fcc* structure, from eqs. (11) and (14) becomes

$$\phi_{\alpha\alpha}(q) = 2(A_1 + B_1)\left[1-\cos\left(\frac{q_\alpha a}{2}\right)\times\left[\cos\left(\frac{q_\beta a}{2}\right)+\cos\left(\frac{q_\gamma a}{2}\right)\right]\right], \quad (16)$$

$$\phi_{\alpha\beta}(q) = 2(A_1 - B_1)\left[\sin\left(\frac{q_\alpha a}{2}\right)+\sin\left(\frac{q_\beta a}{2}\right)\right], \quad (17)$$

where $\alpha \neq \beta \neq \gamma$ and a is lattice parameter. Similarly, eq. (10) at the 1NN shell of impurity, gives

$$F_\alpha(q) = i2\sqrt{2}F_I \sin\left(\frac{q_\alpha a}{2}\right)\left[\cos\left(\frac{q_\beta a}{2}\right)\cos\left(\frac{q_\gamma a}{2}\right)\right], \quad (18)$$

where F_I is the force acting on the 1NN sites of impurity. Considering the interaction with the 2NN shell, the components of $F(q)$ are

$$F_\alpha(q) = i2F_{II}\sin(q_\alpha a), \quad (19)$$

where F_{II} is the force at the 2NN site of impurity.

With the knowledge of $\phi_{\alpha\beta}(q)$ and $F_\alpha(q)$, one can solve eq. (13) for $Q(q)$ using the properties of determinants. For the radial forces at the 1NNs shell only (usually called the F_I system) of the impurity,

$$iQ_1(q) = \frac{\sqrt{2}F_I}{NA_1}\frac{\begin{vmatrix}\sin x(\cos y+\cos z) & G_2 & G_3\\ \sin y(\cos z+\cos x) & G_{22} & G_4\\ \sin z(\cos x+\cos y) & G_4 & G_{33}\end{vmatrix}}{\Delta}, \quad (20)$$

where $\Delta = \begin{vmatrix}G_{11} & G_2 & G_3\\ G_2 & G_{22} & G_4\\ G_3 & G_4 & G_{33}\end{vmatrix}$, (21)

$$G_{11} = \left[1+\frac{B_1}{A_1}\right]\left[2-\cos x(\cos y+\cos z)\right], \quad (22)$$

$$G_2 = \left[1-\frac{B_1}{A_1}\right]\sin x\sin y, \quad (23)$$

$$G_3 = \left[1-\frac{B_1}{A_1}\right]\sin x\sin z, \quad (24)$$

$$G_4 = \left[1-\frac{B_1}{A_1}\right]\sin y\sin z, \quad (25)$$

$$x = \frac{q_x a}{2}, \quad y = \frac{q_y a}{2}, \quad z = \frac{q_z a}{2}. \quad (26)$$

G_{22} and G_{23} are obtained from the expression for G_{11} by cyclic permutation of x, y, z. $Q_2(q)$ and $Q_3(q)$ can be obtained from $Q_1(q)$ using cubic symmetry. For radial forces acting only on the 2NN shell (called F_{II} system) of the impurity,

$$iQ_1 = \frac{F_{II}}{NA_1}\begin{vmatrix}\sin 2x & G_2 & G_3\\ \sin 2y & G_{22} & G_4\\ \sin 2z & G_4 & G_{33}\end{vmatrix}. \quad (27)$$

$Q_2(q)$ and $Q_3(q)$ can be obtained from $Q_1(q)$ using cubic symmetry.

Calculation of F_I and F_{II} :

The external force $F(R_n^0)$ for substitutional impurity in *fcc* host is calculated considering the four configurations as shown in Figure 1. The difference in the potential energies of the (*a*) and (*d*) configurations is

$$\Phi(d)-\Phi(a) = [\Phi(d)-\Phi(c)]+[\Phi(c)-\Phi(b)] + [\Phi(b)-\Phi(a)] = \sum_n\left[\phi_{III}(|R_n|)-\phi_{IIII}(|R_n|)\right] + \frac{1}{2}\sum_{n,n'}\left[\phi_{IIII}(|R_{n'}-R_n|)-\phi_{IIII}(|R_{n'}^0-R_n^0|)\right], \quad (28)$$

where $\phi_{IIII}(r)$ and $\phi_{III}(r)$ are the host-host and impurity-host interaction potentials respectively. Comparing eqs. (2) and (28), the second term of both the expressions is the same;

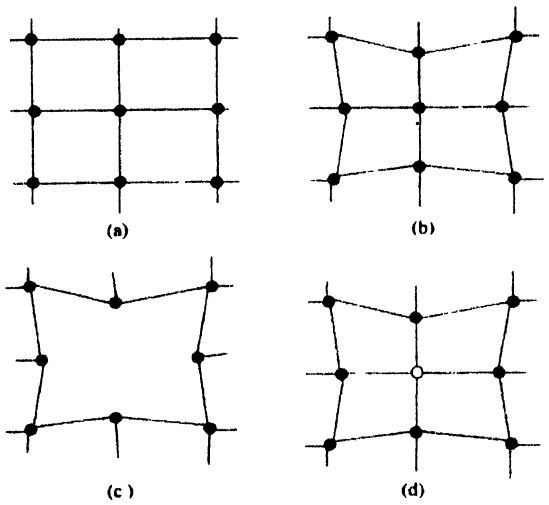

Figure 1. The four configurations of the lattice for substitutional impurity. (a) Perfect host lattice, (b) strained lattice due to external force, (c) strained lattice with one atom removed, and (d) an impurity atom placed at the vacant lattice site

therefore, equating the first term of eqs. (2) and (28), one gets

$$F_\alpha(R_n^0) = -\frac{\partial}{\partial u_\alpha(R_n^0)}\sum_{n'}\Delta\phi(|R_{n'}|), \quad (29)$$

where $\Delta\phi(r) = \phi_{III}(r)-\phi_{IIII}(r)$. (30)

Expanding $\Delta\phi(|\boldsymbol{R}_n^0|)$ in the power series of $\boldsymbol{u}(\boldsymbol{R}_n^0)$, the forces F_I and F_{II} for the central potential are given as

$$F_\alpha(\boldsymbol{R}_n^0) = -\frac{\partial}{\partial r}\Delta\phi\Big|_{|r|=|R_n^0|} - \boldsymbol{u}(\boldsymbol{R}_n^0)\frac{\partial^2}{\partial r^2}\Delta\phi \qquad (31)$$

Eq. (31) can be solved in the two approximations. If $u(R_n^0)$ is very small, the second term in eq. (31) can be neglected. It is called the first approximation where the force constants of the host metal remain unchanged in the presence of the impurity. If $u(R_n^0)$ is significant, both the terms in eq. (31) are retained. It is called the second approximation and takes care of the impurity-induced change in the force constants of the lattice. To include the interactions up to 2NN's, the atomic displacements due to F_I and F_{II} are combined to evaluate $\boldsymbol{u}(\boldsymbol{R}_n^0)$ in the second approximation as done by Kanzaki.

The conduction electrons in the transition metal have both the s and quasilocalized d characters and these characteristics should be included in the calculation of the ion-ion interaction potential. In the formation of TM, d state are broadened into quasilocalized bands, with finite bandwidth. Further, the d bands get distorted due to crystal potential and there is s-d hybridization. These effects are included in the Wills and Harrison transition metal model potential [3] which is given as

$$\phi_{III}(r) = \phi_{III}^{FE}(r) + \phi_{HH}^{c}(r) + \phi_{III}^{b}(r), \qquad (32)$$

where $$\phi_{III}^{FE}(r) = Z_{sII}^2 e^2 \cosh^2(\kappa r_{cII})\frac{\exp(-\kappa r)}{r}, \qquad (33)$$

$$\phi_{HH}^{c}(r) = Z_{dII}\frac{225}{\pi^2}\frac{\hbar^2 r_{dH}^6}{mr^8} \qquad (34)$$

and $$\phi_{HH}^{b}(r) = -Z_{dH}\left|1-\frac{Z_{dII}}{10}\right|\left[\frac{12}{n}\right]^{1/2}\frac{28.1}{\pi}\frac{\hbar^2 r_{dII}^3}{mr^5} \qquad (35)$$

Here, $\phi_{III}^{FE}(r)$ is the free electron contribution, $\phi_{III}^{c}(r)$ arises from the shift in the d band center due to s-d hybridization and ϕ_{III}^{b} arises from the finite d-bandwidth. Z_{sH} and Z_{dH} are the number of s and d conduction electrons per host atom, κ is the Thomas Fermi screening constants, r_{cH} is the Ashcroft model-potential core radius and r_{dII} are the d state radii. n is the number of 1NNs of the host lattice and m is the mass of the electron.

Eqs. (32)–(35) are generalized to write the interatomic potential for the impurity-host interaction in the dilute alloys, which is given as [3]

$$\phi_{IH}(r) = \phi_{III}^{FE}(r) + \phi_{IH}^{c}(r) + \phi_{IH}^{b}(r), \qquad (36)$$

where $$\phi_{III}^{FE}(r) = Z_{sH}Z_{sI}e^2\cosh(\kappa' r_{cH})\cosh(\kappa' r_{cI})\frac{\exp(-\kappa' r)}{r} \qquad (37)$$

$$\phi_{IH}^{c}(r) = Z_d^{\text{eff}}\frac{225}{\pi^2}\frac{\hbar^2 r_{dH}^3 r_{dI}^3}{mr^8} \qquad (38)$$

and $$\phi_{IH}^{b}(r) = -Z_d^{\text{eff}}\left|1-\frac{Z_d^{\text{eff}}}{10}\right|\left[\frac{12}{n}\right]^{1/2}\cdot\frac{28.1}{\pi}\frac{\hbar^2 r_{dII}^{3/2} r_{dI}^{3/2}}{mr^5} \qquad (39)$$

Here, Z_{sI} and Z_d^{eff} are the number of s conduction electrons and effective quasilocalized d-electrons per impurity atom r_{dI} is the d-state radius, r_{cI} is the Ashcroft model-potential core radius for the impurity and κ' is the Thomas Fermi screening length for host-impurity interaction. It is difficult to know the variation of number of d electrons in the d band by the introduction of an impurity. Therefore, we take the effective number of d electrons, Z_d^{eff}, in an alloy as the weighted average of the number of d electrons in the host and impurity atoms, *i.e.*

$$Z_d^{\text{eff}} = C_H Z_{dH} + C_I Z_{dI}, \qquad (40)$$

where Z_{dI} is the number of quasilocalized d electrons per impurity atom and C_H and C_I are the concentrations of host and impurity atoms respectively.

In the alloying process, there may be further transfer of electrons to or from the s and d bands, as a result of which the conduction electron charge would redistribute around impurity to screen or unscreen it. However, we assume that these charge transfers are small and we write the excess interatomic potential due to impurity as

$$\Delta\phi(r) = \Delta\phi^{FE}(r) + \Delta\phi^{c}(r) + \Delta\phi^{b}(r), \qquad (41)$$

where $$\Delta\phi^{FE}(r) = \frac{Z_{sH}e^2}{r}\times\left[Z_{sI}\cosh(\kappa' r_{cH})\cosh(\kappa' r_{cI})\exp(-\kappa' r) - Z_{sH}\cosh^2(\kappa r_{cH})\exp(-\kappa r)\right], \qquad (42)$$

$$\Delta\phi^{c}(r) = \left[Z_d^{\text{eff}} r_{dI}^3 - Z_{dH} r_{dH}^3\right]\frac{225}{\pi^2}\frac{\hbar^2 r_{dH}^3}{mr^8}, \qquad (43)$$

and $$\Delta\phi^{b}(r) = \left[-Z_d^{\text{eff}}\left(1-\frac{Z_d^{\text{eff}}}{10}\right)\left(1-\frac{Z_{dH}}{10}\right)r_{dH}^{3/2}\right]\left[\frac{12}{n}\right]^{1/2}\frac{28.1}{\pi}\frac{\hbar^2 r_{dH}^{3/2}}{mr^5}. \qquad (44)$$

In eqs. (41) to (44), $\Delta\phi^{FE}(r)$, $\Delta\phi^{c}(r)$ and $\Delta\phi^{b}(r)$ are impurity induced changes in the potential due to free electron, s-d hybridization and d-band width contributions respectively.

3. Calculations and results

The above formalism is used to calculate the atomic displacements in Cu dilute alloys due to 3*d* (Co and Ni), 4*d* (Pd and Ag) and 5*d* (Pt and Au) transition metal impurities. The physical parameters and few calculated results are given in Tables 1 and 2. The host potential $\phi_{HH}(r)$ and the impurity host potential $\phi_{IH}(r)$ are used to calculate excess potential $\Delta\phi(r)$ using eq. (41).

Table 1. The physical parameters (in a.u.) of Cu metal. a is the lattice parameter, Ω_0 is atomic volume, Z is number of s and d conduction electrons per atom and A_1, B_1 are force constants as defined in eq. (15).

Host	a	Ω_0	A_1 (10^{-2})	B_1 (10^{-2})
Cu	6.82	76	1.5669	−0.3474

Table 2. r_c and r_d are the Ashcroft core radius and d state radius respectively, F_I and F_{II} (in a.u.) are impurity-induced forces evaluated at 1NN's and 2NN's in the second approximation and E_r is the relaxation energy

			Cu		
Imp	r_c (a.u.)	r_d (a.u.)	$F_I(10^{-3})$	$F_{II}(10^{-3})$	$E_r(-10^{-1}$ eV)
Co	1.55	1.70	3.52	0.21	1.94
Ni	1.00	1.34	1.47	0.08	0.35
Cu	0.87	1.27			
Pd	0.98	1.77	5.83	0.18	0.52
Ag	0.85	1.68	6.10	0.31	5.83
Pt	0.62	1.97	6.67	0.11	7.03
Au	0.76	1.91	7.78	0.36	9.49

The change in potential $\Delta\phi(r)$ due to impurities in Cu metal depends upon impurity induced *s-d* hybridization and shifts in the *d* band center which depends on the difference between Ashcroft core radius and *d*-state radius of the impurity and the host. In the dilute alloys of Cu, $\Delta\phi(r)$ for 3*d* impurities are smaller by an order of magnitude than those for 4*d* and 5*d* impurities. $\Delta\phi(r)$ is repulsive at small distances and becomes attractive at large distances for all the impurities.

The calculated $\Delta\phi(r)$ is used in eq. (31) to calculate F_I and F_{II} at the 1NN and 2NN of impurity in the second approximation. These values of F_I and F_{II} which are sensitive to the slope of $\Delta\phi(r)$ are given in Table 2. In the Cu host, the forces are repulsive at 1NN's and 2 NN's for Co, Pd, Ag, Pt and Au impurities. For Ni impurity, forces are attractive at the 1NN's and repulsive at the 2NN's.

These values of F_I and F_{II}, and the calculated values of force constants A_1 and B_1, are used to calculate $\phi_{\alpha\alpha}(q)$ and hence $Q(q)$ with the help of eqs. (20–27). The inverse Fourier transform of $Q(q)$, as given in eq. (5) gives $u(R_n^0)$.

The numerical calculations are simplified by replacing the sum over q by the integration over the cube of edge $4\pi/a$ which inscribes the first Brillouin zone and using the fact that for any function $F(q)$,

$$\int F(q)\,dq = \frac{1}{2}\int_{\text{cube}} F(q)\,dq \tag{45}$$

for the *fcc* structure. The integration is carried out by Gaussian quadrature method. The calculated values of atomic displacements are tabulated in Tables 3 to 5 for Cu (Co, Ni, Pd, Ag, Pt and Au) dilute alloys respectively. These displacements are oscillatory in nature and are significant even up to twenty nearest neighbors of impurity which are tabulated here.

Table 3. Atomic displacements (in a.u.) of the NN's of Co and Ni impurities in Cu. The coordinates (n_1, n_2, n_3) of the NN's are in units of $(a/2)$ and (u_x, u_y, u_z) are cartesian components of atomic displacements here and in the subsequent tables.

NN's	Co			Ni		
(n_1, n_2, n_3)	u_x	u_y		u_x		
110	0.0353	0.0353	0.0000	−0.0150	−0.0150	0.0000
200	−0.0078	0.0000	0.0000	0.0080	0.0000	0.0000
211	0.0106	0.0118	0.0118	−0.0043	−0.0051	−0.0051
220	0.0164	0.0164	0.0000	−0.0070	−0.0070	0.0000
310	−0.0067	0.0016	0.0000	0.0038	0.0002	0.0000
222	0.0109	0.0109	0.0109	−0.0047	−0.0047	−0.0047
321	0.0063	0.0078	0.0048	−0.0026	−0.0032	−0.0019
400	−0.0075	0.0000	0.0000	0.0029	0.0000	0.0000
411	−0.0052	−0.0004	−0.0004	0.0025	0.0005	0.0005
330	0.0090	0.0090	0.0000	−0.0039	−0.0039	0.0000
420	−0.0027	0.0010	0.0000	0.0015	0.0000	0.0000
332	0.0076	0.0076	0.0060	−0.0032	−0.0032	−0.0024
422	0.0030	0.0034	0.0034	−0.0011	−0.0012	−0.0012
431	0.0041	0.0050	0.0018	−0.0017	−0.0020	−0.0007
510	−0.0044	−0.0009	0.0000	0.0016	0.0004	0.0000
521	−0.0032	−0.0006	−0.0005	0.0015	0.0004	0.0003
440	0.0056	0.0056	0.0000	−0.0024	−0.0024	0.0000
433	0.0054	0.0049	0.0049	−0.0022	−0.0020	−0.0020
530	−0.0008	0.0000	0.0000	0.0005	−0.0002	0.0000
442	0.0051	0.0051	0.0028	−0.0021	−0.0021	−0.0011

In the CuCo dilute alloy, the 1NN's displace away from the impurity, the 2NN's displace towards impurity atom, and third and fourth NN's displace away from the impurity which are followed by oscillatory nature of displacements. The maximum $|u(r)|$ due to Co is found at 1NN's site. For Co impurity, the number of atoms displace away from the impurity are larger than those move towards the impurity atom.

Table 4. Atomic displacements (in a.u.) of the NN's of Pd and Ag impurities in Cu.

NN's	Pd			Ag		
(n_1, n_2, n_3)	u_x	u_y	u_z	u_x	u_y	u_z
110	0.0588	0.0588	0.0000	0.0613	0.0613	0.0000
200	−0.0177	0.0000	0.0000	−0.0152	0.0000	0 0000
211	0.0174	0.0198	0.0198	0.0183	0 0205	0.0205
220	0.0273	0.0273	0.0000	0.0284	0.0284	0.0000
310	−0.0121	0.0017	0.0000	−0.0119	0.0024	0.0000
222	0.0182	0.0182	0.0182	0.0190	0.0190	0.0190
321	0.0103	0.0128	0.0078	0.0108	0.0134	0.0083
400	−0.0122	0.0000	0.0000	−0.0129	0.0000	0.0000
411	−0.0090	−0.0010	−0.0010	−0.0092	−0.0008	−0.0008
330	0.0150	0.0150	0.0000	0.0156	0.0156	0.0000
420	−0.0049	0.0012	0.0000	−0.0049	0.0015	0.0000
332	0.0127	0.0127	0.0098	0.0132	0.0132	0.0103
422	0.0049	0.0054	0.0054	0.0052	0.0058	0.0058
431	0.0068	0.0083	0.0029	0.0071	0.0087	0.0031
510	−0.0070	−0.0016	0.0000	−0.0075	−0.0016	0.0000
521	−0.0054	−0.0011	−0.0009	−0.0055	−0.0010	−0.0008
440	0.0094	0.0094	0.0000	0.0098	0.0098	0.0000
433	0.0089	0.0080	0.0080	0.0094	0 0084	0.0084
530	−0.0015	0.0013	0.0000	−0.0014	0.0015	0.0000
442	0.0084	0.0084	0.0045	0.0088	0.0088	0.0048

Table 5. Atomic displacements (in a.u.) of the NN's of Pt and Au impurities in Cu.

NN's	Pt			Au		
(n_1, n_2, n_3)	u_x	u_y	u_z	u_x	u_y	u_z
110	0.0674	0.0674	0.0000	0.0782	0.0782	0.0000
200	−0.0229	0.0000	0.0000	−0.0202	0.0000	0.0000
211	0.0198	0.0227	0.0227	0.0233	0.0262	0.0262
220	0.0313	0.0313	0.0000	0.0363	0.0363	0.0000
310	−0.0144	0.0015	0.0000	−0.0154	0.0029	0.0000
222	0.0210	0.0210	0.0210	0.0242	0.0242	0.0242
321	0.0118	0.0145	0.0089	0.0138	0.0171	0.0105
400	−0.0138	0.0000	0.0000	−0.0164	0.0000	0.0000
411	−0.0105	−0.0013	−0.0013	−0.0118	−0.0011	−0.0011
330	0.0172	0.0172	0.0000	0.0199	0.0199	0.0000
420	−0.0058	0.0011	0.0000	−0.0063	0.0019	0.0000
332	0.0145	0.0145	0.0112	0.0169	0.0169	0.0132
422	0.0055	0.0061	0.0061	0.0066	0.0073	0.0073
431	0.0078	0.0094	0.0033	0.0091	0.0111	0.0040
510	−0.0079	−0.0019	0.0000	−0.0095	−0.0021	0.0000
521	−0.0062	−0.0014	−0.0011	−0.0071	−0.0014	−0.0011
440	0.0108	0.0108	0.0000	0.0124	0.0124	0.0000
433	0.0102	0.0091	0.0091	0.0120	0.0107	0.0107
530	−0.0018	0.0014	0.0000	−0.0019	0.0019	0.0000
442	0.0096	0.0096	0.0051	0.0112	0.0112	0.0061

In CuNi, the (310), (321) and (411) NN's show the anisotropic displacements and atomic displacements due to Ni impurity. For Ni impurity, the displacements of NN's which move towards the impurity are larger than those which move away from the impurity; therefore, the lattice contracts. The displacements due to Pd and Ag impurities are isotropic as well as anisotropic. The $|u(r)|$ is maximum at 1NN's and behavior of NN's are similar to Co impurity. The behavior of Pt and Au impurities is similar to that of Pd and Ag impurities. The maximum displacement occurs at the 1NN and is displaced away from the impurity.

The magnitude of atomic displacements for Cu alloys up to 5NN's are shown in Figure 2. The strain field decreases with the increase in *d*-electrons for 3*d* impurities *i.e.* from Co to Ni. For 4*d* impurities also the strain increases from Pd to Ag impurity. Similar trend is found for the strain field due to 5*d* impurities Pt and Au. The maximum displacement of 2.3% of R_1^0 is found for CuAu alloy while minimum displacement of 0.43% of R_1^0 is for CuNi alloy.

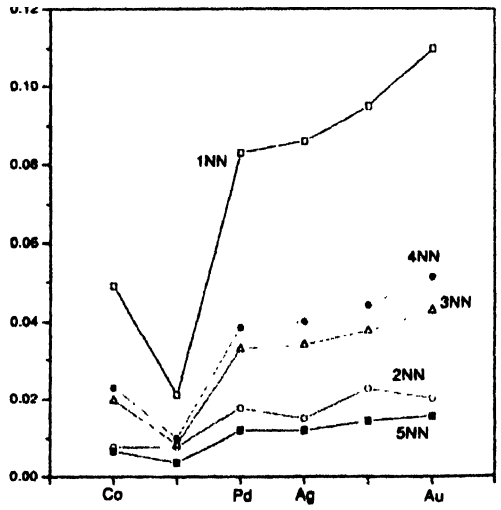

Figure 2. The atomic displacements of the 5NN's of the Co, Ni, Pd, Ag, Pt and Au impurities in Cu host. The solid lines joining are for visual guidance.

The calculated atomic displacement of the 1NN's for Pd, Ag, Pt and Au impurities in Cu show lattice expansions of 0.0832 a.u., 0.0867 a.u., 0.0953 a.u. and 0.11057 a.u. at 1NN's, whereas corresponding experimental observations show lattice expansions of 0.0718 ± 0.0076 a.u., 0.115 ± 0.0132 a.u., 0.0737 ± 0.00945 a.u. and 0.0907 ± 0.0076 a.u. respectively [1]. The calculated $u(r)$ at 1NN due to Ni impurity, shows contractions of 0.0208 a.u. at the 1NN's while the experimental results show the contraction of 0.0321 ± 0.023 at 1NN's [1]. For Co impurity, calculated $u(r)$ gives expansion of 0.0499 a.u. at the 1NN's whereas the experimental value at the 1NN's is 0.00567 ± 0.034 (*i.e.* varies from the contraction of 0.028 a.u. to expansion of 0.0397 a.u.) [1].

Due to large error bars in the experimental values as shown in Figure 3, the exact comparison remains inconclusive, however the calculated and experimental results are in good qualitative agreement.

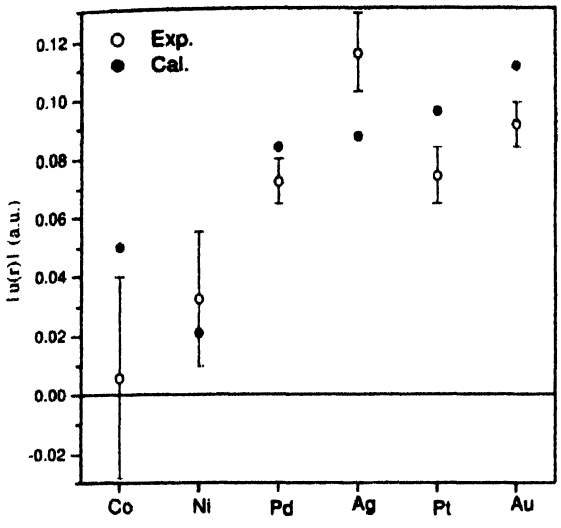

Figure 3. The magnitude of the displacement $|u(r)|$ is compared with the experimental value for Co, Ni, Pd, Ag, Pt and Au impurities in Cu.

The calculated atomic displacements up to 2NN's are used to calculate the impurity induced relaxation energy E_r which is given as

$$E_r = -\frac{1}{2}\sum F_{n\alpha} u_n \tag{46}$$

Here, F is isotropic and the values of F_I and F_{II} tabulated in Table 2 are used in eq. (46). The result for E_r are also given in Table 2. The relaxation energies for Ni and Pd are smaller than other impurities, therefore these impurities may be easily dissolved in Cu. However, in case of Pt and Au, the relaxation energies are larger than other impurities, and these may not easily be dissolved in Cu.

4. Discussion

We have used here Wills and Harrison model potential [7] for the host Cu metal and other transition metal impurities. The effect of partially localized *d*-electrons is included through *d* band width and *s-d* hybridization. The host potential $\phi_{HH}(r)$ and change in potential due to impurity $\Delta\phi(r)$ are very small and smooth beyond 2NN distance, therefore the contribution to $\phi_{\alpha\beta}(q)$ and $F_\alpha(q)$ are expected to be small beyond 2NN's. In the present calculations, it is assumed that the impurity is screened by Fermi-Thomas screening, therefore Fridel oscillations are absent. In the numerical calculations, the cubic symmetry of the lattice is retained although the exact anisotropy of the Brillouin Zone is not accounted for. This may not introduce serious error considering other simplifications in the calculations.

The displacements compared with the XAFS results, show that calculated displacements are in close qualitative agreement with the experimental values, considering the error bars in the calculations. *d* charge of the dilute alloys has been approximated as effective charge in our calculations. It is always difficult to estimate the transfer of *d* charge in transition metal based alloys. The more accurate value of effective *d* charge would certainly improve the atomic displacements. The tabulated values of displacements may be quite useful to investigate heat of solution, electric field gradients, asymmetry parameter, wipe out number, Knight shift and other properties of the defect lattice where impurity induced displaced positions of the host atoms in dilute alloys of Cu are needed. This will help in basic understanding of the alloy formation. Further, these study will explain the strength at high temperature, high stiffness, low coefficient of thermal expansion and chemical compatibility in a variety of environments.

Acknowledgment

The financial support from University Grants Commission (UGC), New Delhi is gratefully acknowledged.

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